

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C08J 9/30, B32B 27/30	A1	(11) International Publication Number: WO 88/ 09801 (43) International Publication Date: 15 December 1988 (15.12.88)
(21) International Application Number: PCT/US87/02459 (22) International Filing Date: 28 September 1987 (28.09.87) (31) Priority Application Number: 056,508 (32) Priority Date: 1 June 1987 (01.06.87) (33) Priority Country: US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor: ERICKSON, Robert, E. ; 5413 Nurmi, Midland, MI 48640 (US). (74) Agent: DAMOCLES, Nemia, C.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AU, BE (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: FOAMED POLYMERIC MATERIALS AND METHOD FOR PREPARING THE SAME (57) Abstract A water absorbent material, in the form of a foam, which has a functionally effective amount of a preneutralized hydrophilic polymer capable of having a water-swellaable character, and a blowing agent. Such a water absorbent material is prepared by contacting a solution of the hydrophilic polymer having a water-swellaable character and a blowing agent, and then heating the composition until it is foamed.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

FOAMED POLYMERIC MATERIALS AND
METHOD FOR PREPARING THE SAME

5

The present invention relates to polymeric materials and, in particular to those polymeric materials which are employed in the form of a foam.

10

Water-swellaable hydrophilic polymers are useful as absorbents for aqueous-based fluids. Examples of such polymers and uses thereof are disclosed in U.S. Patent Nos. 3,926,891; 4,190,562; 4,293,609 and 4,424,247. Examples of disposable absorbent articles

15

containing water absorbent polymers are disclosed in U.S. Patent No. 3,888,257.

20

It has been common practice to employ high molecular weight, water-swellaable hydrophilic polymers in water absorbent applications. Such high molecular weight polymers provide desirable properties such as increased water absorbency and water retention and high gel strengths.

25

-2-

Contacting water-swellaable polymers with a blowing agent is described in the prior art. U.S. Patent 4,415,388 to Korpman teaches a process for producing an absorbent-bearing foam product. The process comprises the steps of feeding into an extruder and subsequently passing through the extruder barrel the following components: a particulate water-insoluble, water-swellaable absorbent polymer having a gel capacity of at least ten; a liquid polyhydroxy organic compound; and a blowing agent. The polyhydroxy organic compound is a high boiling liquid such as glycol and is the medium in which to disperse the polymeric absorbent and the foaming generator. After the extruder, the resultant mixture is passed into a die at elevated temperatures to cause foam formation and subsequently expelling the foam onto a substrate.

The problem with the process taught by Korpman is that the liquid polyhydroxy organic compound comprises a substantial portion of the final composition and is non-absorbent and water sensitive. The fluid portion is the polyhydroxy compound in the mixture and is not volatile when the compound is foamed. Commercially, this is not advantageous because the final compound is soft and sticky, which makes it difficult to handle in end use applications.

U.S. Patent No. 4,529,739 to Scott et al. teaches an artisan to contact an aqueous polymer dispersion, said polymer capable of having a water-swellaable character and containing a functional amount of pendant acid moieties in acid form, with a carbon dioxide-yielding compound decomposable blowing agent which is capable of neutralizing an effective amount of pendant acid moieties. While the process taught by

-3-

Scott et al. represents one possible solution to preparing polymeric materials which can be easily formulated, the carbonate blowing agent requires careful processing conditions to obtain a uniform and controlled foaming of the polymer. It is desirable to avoid the problems associated with preparing foamed polymeric absorbent materials which require the use of a blowing agent as a neutralizing agent.

In view of the deficiencies of the prior art, it would be highly desirable to provide a process for preparing polymeric materials which can be easily formulated for use in applications such as those involving the absorption of aqueous fluids.

The present invention is a material capable of absorbing aqueous fluids which material comprises, in the form of a foam, an amount of a preneutralized hydrophilic polymer capable of having a water-swella-
ble character.

In another aspect, the present invention is a process for preparing a foamed water-swella-
ble polymeric water absorbent material, said process comprising contacting a solution of a preneutralized hydrophilic polymer capable of having a water-swella-
ble character and a blowing agent, and then heating the composition until it is foamed.

The foamed absorbent product provides a structure with increased surface area and greater porosity than a comparable weight of absorbent in a solid film or sheet form. Such foam structures permit greater fluid penetration with decreased gel blocking. Also, such structures provide greater air permeability

-4-

for better comfort in personal care products and less flow restriction in filtration applications. Products of this invention are generally a softer feeling product, and thus are useful as absorbent layers or foamed particulates in personal care absorbent products such as, for example, feminine sanitary napkins, adult incontinent pads, bed pads and baby diapers. Such compositions are useful as water collecting and holding media in filters, horticultural and agricultural applications.

As is required in the process of this invention, these polymers contain a functionally effective amount of acid moieties in generally neutralized form. By "preneutralized" is meant that the polymer has acid moieties pendant from said polymer backbone which are in generally neutralized form. Therefore, the pH of the polymer solution will generally be basic, e.g., 7.0 or higher. Typically, the amount of acid moieties in acid form varies to less than 1 weight percent, based on the monomers containing acid moieties which are polymerized to form the polymer.

Preneutralized water-swellaable, hydrophilic polymers employed in this invention are readily prepared by those of ordinary skill in the art. The polymers employed initially have pendant acid moieties in acid form which are neutralized when the polymer is mixed with an aqueous alkaline solution. A general description of a method suitable for the preparation of said preneutralized polymers is set forth in U.S. Patent No. 4,026,932; issued in 1977 to Gross et al.

-5-

For the purpose of this invention, a moisture absorbent or water-swella-
ble polymer or polyelectrolyte is defined as one that absorbs several times its weight of water. The amount of water which a particular
5 polymer will absorb (i.e., the water absorbent capacity) is dependent upon the pH of the aqueous medium which is being absorbed, the molecular weight of the polymer, the amount of ionic character of the polymer, and the amount of crosslinking in the polymer.
10

In addition, for purposes of this invention, a polymer capable of having a water-swella-
ble character is that polymer which can be modified (e.g., by hydrolysis) in order to provide a water-sensitive
15 character. Thereafter the polymer is made water-swella-
ble, for example, by lightly crosslinking it.

Generally, the polymer employed will be selected from the same group of water-swella-
20 ble polymers, but the polymer may be in a lightly cross-linked form or may be in a high molecular weight form.

In one embodiment, suitable water-swella-
25 ble hydrophilic polymers can be lightly crosslinked or are capable of being lightly crosslinked. When employing the polymer in crosslinked form, the polymer will be crosslinked sufficiently to maintain the cellular structure of the foam during processing but will not be
30 crosslinked to an extent to interfere with further processing steps. Preferably, the viscosity of the hydrophilic polymer, before lightly crosslinking at 25 percent solids, is at least 10,000 centipoise (10 Pascal-second); most preferably, up to 20,000
35 centipoise (20 Pascal-second).

-6-

Crosslinking agents which are used in an effective amount to lightly crosslink the polymer may be the difunctional or polyfunctional crosslinking agents.

5

Illustrative examples of the difunctional agents useful in this invention are polyhaloalkanols such as 1,3-dichloroisopropanol; 1,3-dibromoisopropanol; sulfonium zwitterions such as the
10 tetrahydrothiophene adduct of novolac resins; haloepoxyalkanes such as epichlorohydrin, 2-methyl epichlorohydrin and epiiodohydrin; polyglycidyl ethers such as 1,4-butanediol diglycidyl ether, glycerine-1, 3-diglycidyl ether, ethylene glycol diglycidyl ether,
15 propylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, polypropylene glycol diglycidyl ethers having an epoxy equivalent weight range of from 175 to 380, bisphenol
20 A-epichlorohydrin epoxy resins having an epoxy equivalent weight range of from 182 to 975 and mixtures of the foregoing.

Illustrative examples of the polyfunctional
25 crosslinking agents useful in this invention are set forth in U.S. Patent Nos. 2,926,154; 3,224,986; and 3,332,901. These polyfunctional crosslinking agents are generally known as polyamide-polyamine epichlorohydrin adducts. One crosslinking agent of
30 this type is commercially available from Hercules Incorporated which is identified either as Kymene 557 or Polycup 172. The structure of these adducts has been discussed in an article by M. E. Corr et al.,
Journal of Applied Polymer Science, vol. 17, pages 721-
35 735 (1973).

-7-

In another embodiment, the water-swellable hydrophilic polymer can be of sufficient molecular weight to maintain its cellular structure during the foaming operation described above. That is, upon being subjected to temperatures sufficient to activate the blowing agent and the foaming of the composition, the molecular weight of the polymer is such that the viscosity of the composition is not significantly reduced. The viscosity of the hydrophilic polymers at 25 percent solids is greater than 20,000 centipoise (20 Pascal second).

Suitable polymers useful in this invention include polyelectrolytes such as ammonium or alkali metal salts of homopolymers and copolymers of aliphatic acids such as, for example, acrylic, methacrylic acid and itaconic acid. Examples of suitable monomers useful in preparing polymers, and copolymers are disclosed in the aforementioned U.S. Patent No. 4,424,247.

Further, the polyelectrolytes can be ammonium or alkali metal salts of homopolymers and copolymers of aliphatic acids copolymerized with derivatives of ethylenically unsaturated acids such as carboxylic acid and sulfuric acid. Exemplary derivatives of ethylenically unsaturated carboxylic acids include C₁₋₄ esters of acrylic acid, polyacrylamide and interpolymers of acrylamide with one or more ethylenically unsaturated copolymerizable copolymers. Such hydrophilic polymers include starch/graft copolymers such as, for example, the water-insoluble alkali salt of saponified, gelatinized starch/polyacrylonitrile graft polymers. Examples of suitable monomers and polymers are disclosed in U.S. Patent No.

-8-

3,997,484. Especially preferred polymers are disclosed in U.S. Patent Nos. 4,117,184; 4,176,667; 4,293,609; and 4,424,247.

5 Also suitable for use in this invention are polymers comprising polymerized sulfonate monomers which can be used in place of or in addition to the monomers that are disclosed in U.S. Patent Nos. 4,117,184; 4,176,667; 4,293,609; and 4,424,247.

10 Examples of suitable water-soluble, ethylenically unsaturated sulfonate monomers include N-sulfoalkyl, α,β -ethylenically unsaturated amide salts such as the alkali metal salts of 2-acrylamido-2-methylpropane sulfonic acid, 2-acrylamido propane sulfonic acid, 2-

15 acrylamido ethane sulfonic acid as well as other such monomers listed in U.S. Patent No. 3,692,673; salts of sulfoalkyl esters of unsaturated carboxylic acids such as alkali metal salts of 2-sulfoethyl methacrylate and

20 other such sulfoalkyl esters as listed in U.S. Patent No. 4,075,134; salts of sulfoarylalkenes such as, for example, vinylbenzyl sulfonic acid and the various salts of vinylbenzyl sulfonate, p-styrene sulfonic acid, and salts of sulfoalkenes such as vinyl sulfonic

25 acid. Of the foregoing sulfonate monomers, the sulfoalkyl derivatives of acrylamide, methacrylamide and sulfoethyl methacrylate are preferred; with those of acrylamide being especially preferred, particularly the sodium and potassium salts of 2-acrylamido-2-

30 methylpropane sulfonic acid (AMPS), and 2-acrylamido-2-propane sulfonic acid. In the most preferred embodiments, the sulfo group is employed in the form of an alkali metal sulfonate such as sodium sulfonate.

35 The blowing agent in the foamable absorbent compositions may be any nongaseous agent which

-9-

decomposes to form gas. Examples of suitable blowing agents include sodium bicarbonate, p-toluene sulfonyl hydrazide and azodicarbonamide. Such blowing agents are those which can release gases such as, for example, nitrogen and carbon dioxide.

The compositions may further comprise surface active agents. Typically, such surface active agents are surfactants that increase the wettability of the final dry absorbent product. Typically, anionic and/or nonionic surfactants can be employed. Examples of useful surfactants are the sodium alkyl sulfonates and the ethylene oxide derivative of alkylated phenols.

Additionally, softening agents may be advantageously employed herein. Examples of useful softening agents are the aliphatic hydroxyl compounds having a boiling point of at least 100°C. Useful aliphatic hydroxyl compounds include aliphatic polyols or derivatives thereof. Representative compounds include ethylene glycol, propylene glycol, the methyl, ethyl, propyl, butyl, or aryl ether of ethylene glycol, ethylene glycol monoacetate and glycerine diacetate. A preferred softening material is glycerine.

In another aspect, this invention relates to a method for making the aforementioned compositions. In one embodiment, said compositions may be prepared by admixing the high molecular weight polymer in wet form, and the blowing agent.

In another embodiment, said compositions are provided by admixing the polymer that is lightly crosslinked or capable of being lightly crosslinked, in

-10-

wet form, the crosslinking agent, and the blowing agent.

5 In either aspect of preparing the composition of this invention, the surfactants and/or softening agents may be mixed with the polymer prior to heating.

10 Processing temperatures will vary depending on the type of blowing agent which is employed, the type of curing agent, as for example crosslinking agent, and the nature of the polymeric functional groups. The composition will be heated until it is foamed. The process of this invention is economically advantageous, because the foaming operation is controllable. When 15 the composition is heated, water removal begins to occur. If a crosslinking agent is present, crosslinking begins, which increases the viscosity of the wet composition. When the activation temperature of the blowing agent is reached, foaming will begin. The 20 foaming is gradual because the temperature of the composition is relatively low until the moisture is removed.

25 Foams of this invention are soft, low density foams. By "foam" it is meant that a sufficient volume of gaseous material is present in the composition such that the surfaces of the gas bubbles contact each other in an open or a closed cell structure. The foam 30 density is approximately 0.2 grams per cubic centimeter (200 kg/m^3) and the capacity in 1 percent sodium chloride solution is 45 grams per gram with a gel strength of 3.3 lb. per square inch (22.8 kPa). Compositions can have closed cell or open cell 35 structures or a structure having a mixture of open and closed cells. The foam structure is dependent upon the

-11-

blowing agent and the processing conditions which are employed.

5 The amounts of active ingredients employed in this invention can vary. Typically, the amount of polymer ranges from 60 to 80 parts by weight of the active ingredients employed. The amount of surfactant ranges from 0 to 10 parts by weight. If employed, the amount of crosslinker ranges from 0.1 to 5 parts by weight of the active ingredients employed. If employed, the amount of softening agent will optimally be in a range of from 20 to 40 parts by weight and the amount of blowing agent will optimally be in a range of from 1 to 10 parts by weight of the active ingredients employed.

20 Foamed polymeric materials of this invention are generally low density, highly porous open cell structures which can be flexible. In some cases the foamed material may contain mixtures of open and closed cell structures. The foamed polymeric materials of this invention can be applied to various substrates and further dried.

25 The compositions of this invention can be attached to a wicking or nonwicking substrate. This may be accomplished by first casting or extruding the composition on a heated or heatable release substrate, followed by curing and drying the foam composition, and then forming a laminate as described in U.S. Patent No. 4,117,184. Alternatively, this may be accomplished by applying the absorbent foam composition directly to the above-mentioned substrates.

35

-12-

The process can be varied to incorporate the compositions of this invention to more than one layer of a wicking or nonwicking substrate to form film laminates and other such materials as those described, for example, in U.S. Patent Nos. 4,117,184; 4,176,667; 4,293,609 and 4,424,247. Further, thoroughly mixed polymer compositions can be incorporated on wicking substrates as described in U.S. 4,117,184 or in the wicking substrates and treated as described in U.S. Patent No. 4,293,609. Such materials exhibit high water absorbent capabilities.

The following examples are presented to further illustrate but not limit the scope of this invention. All parts and percentages are by dry weight of the active ingredients employed.

Example 1

Into a glass container were mixed 27 parts glycerine, 1 part of a polyamide-epichlorohydrine resin crosslinking agent sold commercially as Polycup® 172, 1 part of a polyethylene glycol ether of a secondary alcohol sold commercially as Tergitol® 15S9 and 5 parts of a P,P'-oxybis-(benzenesulfonyl hydrazine) blowing agent in contact with 71 parts of an acrylic polymer solution. The acrylic polymer was an acrylate copolymer having approximately 50 mole percent ethyl acrylate, approximately 33 mole percent sodium acrylate and approximately 17 mole percent sodium methacrylate. The polymer had a molecular weight of 10^6 and was present in solution at 26.0 weight percent. The components were mixed together to form a composition. A 30 mil (0.76 mm) wet film of the composition was cast upon a release coated glass plate preheated to between

-13-

250° (120°) and 300°F (150°C). The plate and film were placed in a hot air circulating oven at a temperature of 325°F (165°C) for approximately 5 minutes. The foamed absorbent polymer was removed from the plate and tested. The foam density was 0.2 gram per cubic centimeter (200 kg/m³) and the capacity in 1 percent sodium chloride solution was 45 grams per gram with a gel strength of 3.3 lb. per square inch (22.8 kPa).

10 Example 2

The composition of Example 1 was fed into an extruder and was extruded at room temperature on a moving wicking substrate. The wicking substrate and film were placed in a hot air circulating oven at a temperature of 325°F (165°C) for approximately 5 minutes. The foamed absorbent polymer was removed from the oven and tested. The foam density was 0.2 grams per cubic centimeter (200 kg/m³) and the capacity in 1 percent sodium chloride solution was 45 grams per gram with a gel strength of 3.3 lb per square inch (22.8 kPa).

-14-

1. A water-swellaable polymeric water absorbent material, said material comprising in foamed form a preneutralized hydrophilic polymer capable of having a water-swellaable character.

2. An absorbent material as claimed in Claim 1, wherein the hydrophilic polymer is selected from the group consisting of ammonium or alkali metal salts of homopolymers and copolymers of aliphatic acids; and polymerized water-soluble ethylenically unsaturated sulfonate monomers.

3. An absorbent material as claimed in Claim 2, wherein the aliphatic acid is selected from the group consisting of acrylic acid, methacrylic acid, and itaconic acid.

4. An absorbent material as claimed in any one of the preceding claims, wherein the hydrophilic polymer is a copolymer of the aliphatic acid and a derivative of an ethylenically unsaturated acid selected from the group consisting of carboxylic acid and sulfuric acid.

-15-

5. An absorbent material as claimed in any one of the preceding claims, wherein the hydrophilic polymer is (1) lightly crosslinked or capable of being lightly crosslinked, or (2) lightly crosslinked with a polyfunctional-or difunctional crosslinking agent.

6. An absorbent material as claimed in any one of the preceding claims, wherein the viscosity of the hydrophilic polymer before lightly crosslinking, at 25 percent solids, is at least 10,000 centipoise (10 Pascal-second).

7. An absorbent material as claimed in any one of the preceding claims, wherein said foamed water-swallowable polymeric water absorbent material further comprises a surface active agent and/or a softening agent.

8. An article comprising a laminate of the absorbent material of any one of the preceding claims and one or more layers of wicking substrates or non-wicking substrates.

9. An absorbent pad which comprises the absorbent material of any one of Claims 1 to 7, one or more layers of wicking or non-wicking substrates, a water impermeable bottom sheet and a water permeable face sheet.

10. A process for preparing a foamed water-swallowable polymeric water absorbent material, said process comprising (1) contacting a solution of a preneutralized hydrophilic polymer capable of having a water-swallowable character and a blowing agent, and (2) heating the composition until it is foamed.

AMENDED CLAIMS

[received by the International Bureau on 12 February 1988 (12.02.88)
claims 5-9 amended; other claims unchanged (1 page)]

5. An absorbent material as claimed in Claim 4, wherein the hydrophilic polymer is (1) lightly crosslinked or capable of being lightly crosslinked, or (2) lightly crosslinked with a polyfunctional or difunctional crosslinking agent.
6. An absorbent material as claimed in Claim 5, wherein the viscosity of the hydrophilic polymer before lightly crosslinking, at 25 percent solids, is at least 10,000 centipoise (10 Pascal-second).
7. An absorbent material as claimed in Claim 6, wherein said foamed water-swellaible polymeric water absorbent material further comprises a surface active agent and/or a softening agent.
8. An article comprising a laminate of the absorbent material of Claim 4 and one or more layers of wicking substrates or non-wicking substrates.
9. An absorbent pad which comprises the absorbent material of any one of Claim 4, one or more layers of wicking or non-wicking substrates, a water impermeable bottom sheet and a water permeable face sheet.
10. A process for preparing a foamed water-swellaible polymeric water absorbent material, said process comprising (1) contacting a solution of a preneutralized hydrophilic polymer capable of having a water-swellaible character and a blowing agent, and (2) heating the composition until it is foamed.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/02459

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT CL 4 C08J 9/30; B32B 27/30		
US CL 428/246, 286, 290, 913; 521/72, 149		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	428/246, 284, 286, 290, 913 521/72, 149	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A 4,117,184 (ERICKSON) 26 SEPTEMBER 1978. ENTIRE COLUMNS 5 AND 6, AND COLUMN 7, LINES 5-13	1-4,10
X	US, A, 4,415,388 (KORPMAN) 15 NOVEMBER 1983. ENTIRE COLUMNS 4, 5, 7 AND 8, WITH EXAMPLES 10-12	1-4,10
<p>¹⁶ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
02 DECEMBER 1987	05 JAN 1988	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	W. J. VAN BALEN	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☒ Claim numbers 5-9 . . . because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

non-compliance with PCT Rule 6.4(a); multiple dependent claim 4 cannot serve as a basis for any other multiple dependent claim (5-9).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This international Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the international Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.